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MINISTRY OF SUPPLY

ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT

APPLIED MATHEMATICS & MECHANICS DIVISION

A.R.D.E. REPORT (B) 7/56

The Effect of High Energy X-rays on the Thermal Detonation of Service Lead Azide

J. M. Groocock

T. R. Phillips

Fort Halstead, Kent.

March 1956

A.R.D.E.
Printing Section

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Ministry of Supply

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thermal detonation of service lead azide.

J.M.Groocock, T.R.Phillips (B.6)

Summary

An atomic explosion produces penetrating radiation, apart from its blast and thermal effects, and it is desirable to know the effect of this radiation on conventional armaments. Of particular interest is its effect on the sensitivity of initiators.

Part I of this report is concerned with an investigation of the effect of high energy X-rays (analogous to the γ-rays of an atomic explosion) on the thermal detonation properties of a typical initiator, Service lead azide. Samples of Service lead azide were exposed to the radiation from a million volt generator. The times of heating, at different temperatures, required to produce detonation of these samples were compared with those of unirradiated samples. It was found that the irradiation produced no effect below dosages of 10^6 roentgens, but marked sensitization was produced by a dosage of 7×10^6 r. This is to be compared with a dosage of 10^4 r received at the edge of the complete damage region of an atomic explosion.

Part II includes a general discussion of sensitivity tests and gives reasons which suggest that the thermal detonation results of Part I might completely specify the effect of irradiation on the sensitivity of the samples investigated.

It concludes with a brief discussion of the mechanism of the thermal detonation of lead azide.

Approved for issue:

H.J.Poole, Deputy Director

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Of the neutrons initially produced those escaping from the immediate proximity
[faint text, partially legible] 0.5 per cent of the energy of the bomb i.e. about 1 per cent
[faint text, partially legible]

Part I

1. Introduction

1.1 Object of the work

An atomic explosion produces its major effects by blast and fire and its
action is thus qualitatively similar to conventional high explosive and incendiary
ordnance. However nuclear radiations are produced also and it is desirable to know
what special effects, if any, these will have on conventional armaments,
particularly at distances from an explosion where major damage is not caused by
blast and thermal radiation. The nuclear radiation consists of fission fragments
together with α-particles, β-particles, neutrons and γ-rays but only the latter two
need be considered, the others being of too short a range to be important. The
effect of irradiation on initiating compositions is of particular importance for
it is possible that a major change in sensitivity might be produced by a relatively
small amount of irradiation. Irradiation of an initiator might give (a) immediate
detonation (b) sensitization making handling unsafe (c) desensitization making the
material unusable. It is the general question of the effect of γ and neutron
irradiation on initiating materials with which we are concerned here. We have
selected Service lead azide as a typical initiator suitable for study and have used
high energy X-rays for our irradiation. These are strictly comparable to γ-rays
and their use makes the irradiation of the test material with high dosages
relatively easy. For reasons that will be discussed below some tentative
conclusions about neutron irradiation can also be drawn from the high voltage
X-irradiation results.

1.2 Comparison of the sensitivity before and after irradiation

As noted above, it is variations in the sensitivity of initiators that are of
major importance. Other factors that are not investigated in this work are power
and stability. The method used for comparing the sensitivities of the irradiated
and unirradiated material was to heat samples at known temperatures and measure
the time of heating required to produce detonation. Tests of this type have been
used by other workers (1). Graphs of time to detonation against temperature for
the unirradiated material and the materials irradiated at various dosages were used
for comparison of sensitivity. A discussion of sensitivity tests and the reasons
for the use of this particular test is given in Part II 1.

1.3 γ and neutron radiations produced by an atomic explosion[*]

γ-rays are initially produced by three processes in an atomic explosion
(a) by the fission process (b) by interaction of neutrons with atomic nuclei
(n.γ reactions) (c) by emmission from an atomic nucleus that has been excited by
a neutron. The γ-rays carry about 1 per cent of the total energy liberation of the
explosion, but roughly 99 per cent of this radiation is absorbed by heavy nuclei
in the immediate vicinity of the explosion. A further 1 per cent of the total bomb
energy is liberated as delayed γ radiation by the radioactive decay of fission
fragments and most of this escapes. An approximate estimate is that from a standard
20 K ton. explosion the total γ-ray dosage in an unprotected position at 2,100 feet
is 10^4 Roentgens (the limit for total damage by blast and thermal effects is given
as 2,100 feet). The average energy of γ-rays at distances greater than 3,000 feet
is about 3 Mev.

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[*] Most of the information in sections 1.3 and 1.4 is quoted from,
"The Effect of Atomic Weapons", Chapter VII, (Reference 2.)

Of the neutrons initially produced those escaping from the immediate proximity of the explosion carry 0·03 per cent of the energy of the bomb i.e. about 1 per cent of the escaping γ-ray energy. At 2,100 feet approximately 2×10^{10} fast neutrons with an energy in excess of 3 Mev will strike each square centimetre of surface and 2×10^{11} slow neutrons with energy mainly about 0·2 ev. Neutrons with energy less than 0·2 ev are readily captured by nitrogen and this gives a lower energy limit for neutrons of appreciable range.

1.4 Mechanism of interaction of γ-rays and neutrons with matter

There are three ways in which γ-rays can interact with matter. The most important of these is by Compton scattering where a γ-ray photon interacts with an electron giving up some of its kinetic energy to the electron. The efficiency of a material for Compton scattering is proportional to its electron density. The second method of interaction, the photoelectric effect, is an inelastic collision between the γ-ray photon and an electron, the photon is destroyed and its energy is completely transferred to the electron. The magnitude of the photoelectric effect is proportional to the 5th power of the atomic number of the irradiated material, and is only significant at fairly high photon energies. The third process is pair production; here the γ-ray photon is annihilated and a positron and an electron are produced. This process requires a minimum photon energy of 1·02 Mev.

It is seen that γ-rays initially lose their energy by producing excited electrons and in a solid insulator these will dissipate their excess energy by interaction with other electrons of the lattice. High energy electrons will be able to interact with extranuclear electrons in deep shells, but low energy electrons will be repelled by potential energy barriers and will only interact with the more loosely bound electrons. The secondary and tertiary etc., electrons will continue to interact with further lattice electrons while they have the necessary energy. The nett effect of γ irradiation on an insulator will be to produce a large number of (a) excitons i.e. electrons in an excited state but still bound to their parent ions (b) conduction band electrons i.e. electrons of slightly higher energy moving freely through the periodic field of the lattice (c) positive holes i.e. lattice positions that have lost an electron (d) photoelectrons i.e. electrons with sufficient energy to escape from the lattice. In addition all these electronic effects will have interactions with the phonons of the lattice vibrations, so that much of the energy will finally be dissipated as heat. It is generally agreed that γ-ray irradiation cannot directly change the position of atomic nuclei (3) and changes in nuclear position can only result from a decomposition process initiated by the irradiation. It is well known that for gases a free ion and an electron are produced for every 30 ev of energy initially possessed by the photon, (2, p.234) this being considerably more than the ionisation energy of the gas molecules. For some solids there is evidence that a conduction band electron and a positive hole are produced for every 10 ev of energy of the bombarding photon (4).

The interaction of neutrons with matter is initially by knock-on collisions with the nuclei and is therefore different from that of the γ-ray photons which first interact with the extra-nuclear electrons (3). In collision with a heavy nucleus the neutron will lose little of its energy, but in each collision with e.g. a hydrogen nucleus, it will lose half of its energy and produce a highly energetic proton moving through the solid. This in turn will lose energy by collision with atomic nuclei, by ionisation and excitation of electrons and by thermal interactions with phonons. The concentration of these effects along its path will be much greater than that produced along the path of an electron. Seitz (5) suggests that temperatures of the order of 10,000°K may be produced for a distance of several atomic radii immediately after the passage of an ion. This "hot spot" is not however big enough to produce detonation (6). Neutrons, in addition to the effects produced by γ-rays will produce interstitial ions and lattice vacancies (3). They have the further capacity of taking part in nuclear reactions and of particular interest to us is the $N^{14}(n, p)C^{14}$ reaction given by neutrons of energy less than 0·2 ev (2, page 241). The general evidence is that neutron irradiation does not produce any effect on bulk materials not given by X-rays and γ-rays (7), but it is necessary with lead azide to consider the effect of interstitial ions and vacancies. The $N^{14}(n, p)C^{14}$ reaction might also produce special effects.

1.5 Decomposition of solid azides by irradiation

No quantitative work has been reported in the literature on the effect of pre-irradiation on the sensitivity of initiators to detonation. Ubbelohde (8) found the exposure of Service lead azide to direct sunlight for several hours reduced the time to detonation at any particular elevated temperature and Garner and Gomm (19) found a similar effect for pre-irradiation with ultra-violet light. It was found both by Ubbelohde and by Hawkes and Winkler (1) that a similar permanent sensitization was produced by a period of pre-heating which was insufficient to give detonation. In addition there has been a considerable amount of work on studies of the reaction kinetics of the decomposition produced by irradiation and also some work on the sensitization to subsequent thermal decomposition produced by pre-irradiation. The latter is particularly relevant, for the thermal decomposition and the detonation are likely to be intrinsically similar reactions although their detailed kinetics may be very different.

The decomposition of barium and potassium azides by ultra-violet light irradiation has been studied by Jacobs and Tompkins (9) and by Thomas and Tompkins (10) and the decomposition of sodium and barium azides by 200 volt electrons has been investigated by Groocock and Tompkins (11). Groocock has also examined the decomposition of α-lead azide by ultra-violet irradiation and by 200 volt electron bombardment (12). Heal has studied the decomposition of sodium azide by irradiation with 58 kV X-rays (13). It has been found that pre-irradiation has a marked effect on a subsequent thermal decomposition and here Thomas and Tompkins (14) and Jacobs and Tompkins (15) have investigated the effect of pre-irradiation with ultra-violet light on barium and potassium azides and Groocock and Tompkins (11) the effect of pre-electron bombardment on barium azide. Bowden and Singh (6) have shown that pre-neutron bombardment accelerates the thermal decomposition of lithium azide. Except for potassium azide it was found that a permanent effect was always produced by irradiation and the subsequent thermal decomposition was markedly accelerated. In all cases the reciprocity law was held i.e. the effect was a function of the total irradiation dosage and not of the rate at which this was applied. Groocock and Tompkins expressed their thermal decomposition results at constant temperature in terms of the equation $P = C(t-t_0)^6$ where P was the amount of decomposition which had occurred at time t; C and t_0 were constants. It was found that pre-bombardment of barium azide spread over an area of 1 sq. cm with an electron current of 20 microamps for 30 seconds at a potential of 40 volts increased the value of C by 400 times. Heal found that X-irradiation of sodium azide, gave no immediate evolution of nitrogen but that gas was liberated on dissolving the irradiated material, indicating a "bulk effect".

Throughout it has been emphasised that the effect of irradiation is to produce imperfections in the solid lattice of various kinds (excitons, free electrons, vacancies, interstitial ions etc., and combinations of these); it is the presence of these imperfections which will be responsible for any sensitization of the material after irradiation. Apart from a direct study of decomposition and detonation, information about imperfections can be given by spectroscopy. The spectroscopy of irradiated solids has been studied by many workers but results of particular interest have been obtained from a study of the reflection spectra of sodium azide by Rosenwasser, Dreyfus and Levy (16). These workers followed the absorption bands produced by γ-irradiation and showed that similar bands, but of different relative intensities, were given by thermal or fast neutron irradiation. They are proposing to extend their work to lead azide.

2. Experimental

2.1 Apparatus and procedure

All experiments were carried out on samples of a single batch of well-aged Service lead azide. Service lead azide contains the α form only and the particles are single well shaped crystals of fairly uniform size. The one or two per cent impurity is mainly lead carbonate. The crystals were sieved and the fraction passing through 235 mesh but not through 300 mesh was used; this fraction was shown by microscopic examination to have a rather more uniform particle size than the unsieved material.

Samples of the sieve fraction weighing about 30 mg. were irradiated using a perspex and tufnol jig attached to the 1 MV. X-ray generator, the azide being held in a position about 58 mms from the focus of the X-ray beam. A 1,000 kilovolt potential was used for all irradiations, but most of the X radiation would, of course, have an energy below 1 Mev. The intensity of the radiation at the position of the azide sample was too high to be measured directly by a radiation dosimeter. It was therefore calculated from a measurement made at a greater distance from the focus of the beam, using the inverse square law. Table I gives details of the radiation dosage given to each sample.

Table I

Sample No.	Weight	Appld. Volts	Electron Current	Time of Irradiation	Dosage in Roentgens
1	0·0255g	1000kv	2·5ma	76·8 mins	10^6r
2	0·0258g	1000kv	2·5ma	7 mins 39 secs	10^5r
3	0·0256g	1000kv	2·5ma	46 secs	10^4r
4	0·0245g	1000kv	2·5ma	0·6 secs	10^3r
11	0·0440g	1000kv	3·0ma	66·8 mins	10^6r
22	0·0451g	1000kv	3·0ma	7 hours	$6·35 \times 10^6$r

Measurements of thermal sensitivity were made in the apparatus illustrated in Fig. I. This equipment was designed for use in a study of the mechanism of the thermal detonation of lead azide and is more complex than is necessary to make only the measurements relevant to this work.

The apparatus made of pyrex glass could be pumped out to a pressure of 10^{-6} mms of mercury by means of a conventional pumping system of liquid nitrogen trap, mercury diffusion pump and rotary oil pump. The samples of azide were contained initially in the small glass bucket A and by means of the magnetic device B could be tipped down the guide tube onto the copper block C contained in the furnace D. The tipping mechanism was such that the bucket banged against the support rod, ensuring that no azide stayed in the bucket.

The electric furnace D was controlled by a proportional temperature controller and the temperature of the copper block varied by less than 0·05°C during the course of a measurement. The temperature was measured using a copper constantan thermocouple; the arrangement was such that the hot junction was just beneath the centre of the top surface of the block and the cold junction was in an ice-water bath. The thermocouple was calibrated against a standard mercury thermometer accurate to 0·1°C over the range 295-355°C. Temperature readings throughout are given in terms of the thermo-emf in millivolts and these were found to have a linear relationship with degrees Centigrade such that 16·000 mv = 587·3°K and of slope 1 mv = 16·0°C.

Measurements were made as follows. The B.45 joint E was opened and samples of azide (2·2mg) were weighed into the two glass buckets A (for simplicity Fig. I shows only one bucket). The bucket holder was resealed in the apparatus and the apparatus pumped overnight at a pressure of 10^{-2} mms with the furnace heated to the desired temperature. Before decomposing the azide the apparatus was pumped down to 10^{-6}mms for three hours with liquid nitrogen round the trap F and a solid carbon dioxide/alcohol mixture round the Pirani gauge P. It was found that reproducibility could only be obtained if the pumping conditions were standard for all runs. The first bucket was then tipped, the azide fell onto the copper block and spread evenly over its one inch diameter surface, being retained by the raised edges. The more usual system of lowering a bucket, of relatively high thermal capacity, into the furnace, gives a heat up time of several minutes and, as the time to detonation in these experiments is of the order of a minute, is obviously unsuitable.

For cubic crystals of edge 0·05 mms, if it is assumed that the heat transfer is entirely by conduction from the copper block, 1/100 of the surface of one face of the crystal being in contact with the block, a very rough calculation indicates that the temperature of the crystal will have risen to within 1°C of the block temperature in 3 seconds. Similarly if it is assumed that the heat transfer is entirely by radiation and black body conditions are used, it is found that it again takes about 3 seconds to reach within 1°C of the furnace temperature. It is possible that, even under the vacuum conditions present, a considerable fraction of the heat transfer might be by gas conduction so that an effective heat up time of the order of 1 second is to be expected. As a large fraction of the heat transfer is by radiation it is necessary for the azide reaction to take place in an enclosure, radiating at the required temperature, in addition to being in contact with the metal block and this was ensured by having the block well inside the furnace. It is of interest to note that in some experiments in which the azide sample was placed upon the heated block, but was free to radiate to a surface at room temperature above it, it was found that the azide temperature was some tens of degrees below that of the block.

On being heated to the reaction temperature the azide immediately began to decompose, nitrogen gas being evolved. Because of the constriction F in the pumping line there was a pressure build up in the reaction chamber and this was measured by the very sensitive Pirani gauge and recorded photographically with a time resolution of better than 1 second. The size of constriction, pumping rate and pressure ranges used were such that the Pirani gauge reading was directly proportional to the rate of decomposition of the azide, but as the quantitative dependence was not necessary for this work it will not be discussed further here. Typical photographic records are shown in Fig. II; A indicates the time at which the azide was inserted, B a typical peak in the decomposition curve and C the point at which detonation occurs. The time t is the "time to detonation" used in later analyses. Thermocouple readings were recorded continuously throughout the run. It should be noted that detonation of single crystals of Service lead azide would produce an immediate pressure pulse of greater than 10^{-4} mms in the reaction chamber, which was quite sufficient to register as a detonation on the record trace. Usually propagation to the rest of the azide took place but when this did not occur the pressure pulse for the first crystal detonating was used in measuring the time to detonation.

When the reaction was complete and the apparatus had once more reached equilibrium a further run was carried out by tipping the second bucket.

2.2 Results

The unirradiated service lead azide was white in colour and there was little change in the appearance of the samples irradiated at dosages of less than 10^6r. The samples irradiated at 10^6r were coloured light brown and those irradiated at 6·35 x 10^6r were coloured dark brown. This indicates the production of additional absorption bands in the visible spectrum, due to the production of high concentrations of imperfections.

The unirradiated service azide was found to detonate at temperatures above 312°C; below this temperature 100 per cent decomposition would occur without detonation. (It had been found previously (17) that pure α-lead azide of particle size 60-150 mesh detonated at temperatures above 285°C). At temperatures only slightly higher than 312° there was a temperature range in which detonation did not always occur. The results for the unirradiated azide are summarised in Figure III where time to detonation is plotted against temperature. It is seen that the time to detonation increases from about 0·55 mins at 317°C to a maximum of about 0·85 mins at 312°. For a few runs in which the standard pumping procedure was not adopted it was found that prolonged evacuation resulted in a reduction in the time to detonation for any given temperature, but this was not systematically investigated.

The results obtained from sample (2) (irradiated at 10^5r) are graphed in Figure III and show no marked difference from the unirradiated sample. The samples (1 and 11) irradiated at 10^6r again show little difference from the unirradiated samples, but there did seem to be more failures to detonate at temperatures above the minimum and there was one run in which detonation occurred after 1.6 mins - other runs had always detonated in less than 1·3 mins or given no detonation.

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A marked difference between sample 22 (irradiated at $6 \cdot 35 \times 10^6 r$) and the other samples was found. The initial peak in the decomposition rate/time curve (Fig. IIB) although still present, is largely obscured by the more rapid acceleration of the later stages of the decomposition. The time to detonation/temperature graph is given in Figure IV and it is seen that at a given temperature the time to detonation is roughly one fifth of that of other samples at the same temperature. Moreover the minimum temperature for detonation is lowered by 15°C to 297°C, the time to detonation at the limit being about $1 \cdot 05$ minutes. Both the time to detonation at a given temperature and the minimum temperature at which detonation can be produced, are important criteria in defining the sensitivity of the material and by both criteria considerable sensitization of the material has been produced by irradiation of this magnitude.

An interesting point is that for the pure α-lead azide of particle size 60-150 mesh (reference 17) at the lowest temperature detonation would occur after heating times as long as 13 minutes. On the other hand in the temperature range studied for the Service azide, the time to detonation for the pure azide seemed approximately the same as that of the Service azide. This is to be investigated further.

3. <u>Discussion</u>

The absorption process for γ-rays or high energy X-rays can be shown to follow an exponential law (2), the transmitted intensity being defined by:

$$I = I_0 \exp(-\mu x)$$

where I_0 is the incident intensity, I the intensity at a depth x and μ the absorption coefficient of the material. μ can be expressed as the sum of the μ's for the different modes of adsorption

i.e. $\mu(\text{total}) = \mu(\text{Compton}) + \mu(\text{photoelectric}) + \mu(\text{pair production})$

$\mu(\text{pair production})$ is zero in our case and as it is known that $\mu(\text{Compton})$ α atomic number of the element and $\mu(\text{photoelectric})$ α (atomic number)^5 we can calculate the absorption coefficient of lead azide from known values of the absorption coefficients of the elements. The X-radiation from the million volt generator will embrace a wide range of energies and for the purpose of calculation a value of 650kV will be used.

For 650 kV X-rays $\qquad \mu(\text{total})$ Al = $0 \cdot 20$)
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$) Reference 2.
$\qquad\qquad\qquad\qquad\qquad \mu(\text{total})$ Pb = $1 \cdot 00$)

Assuming that for aluminium μ total = μ Compton the value of μ Compton for lead can be calculated

$$\mu(\text{Compton}) \text{ Pb} = \mu(\text{Compton}) \text{ Al} \times \frac{\text{no. of electrons/cc Pb}}{\text{no. of electrons/cc Al}}$$

$$= 0 \cdot 20 \times \frac{27}{13 \times N \times 2 \cdot 70} \times \frac{82 \times N \times 11 \cdot 34}{207}$$

$$= 0 \cdot 69$$

Where N is Avagadro's number, $2 \cdot 70$ and $11 \cdot 34$ are the densities of aluminium and lead respectively, 27 and 207 are their atomic weights, and 13 and 82 are their atomic numbers. From this $\mu(\text{photoelectric})$ for lead is $1 \cdot 00 - 0 \cdot 69 = 0 \cdot 31$ in good agreement with the graph given in Reference 2 page 226.

$\mu(\text{Compton})$ for single crystals of lead azide (density $4 \cdot 70$) is calculated similarly. 291g of PbN_6 contain $82N + 6 \times 7N = 124N$ electrons

$$\mu(\text{Compton})PbN_6 = \mu(\text{Compton})Pb \ \frac{\text{no. of electrons/cc } PbN_6}{\text{no. of electrons/cc } Pb}$$

$$= 0 \cdot 69 \times \frac{124N \times 4 \cdot 70}{291} \times \frac{207}{82N \times 11 \cdot 34}$$

$$= 0 \cdot 31$$

$\mu(\text{photoelectric})$ is negligible for nitrogen and we therefore need only consider the absorption due to the lead atoms in the azide.

$$\mu(\text{photoelectric})PbN_6 = \mu(\text{photoelectric}) \ Pb \times \frac{\text{no. of atoms of Pb/cc in } PbN_6}{\text{no. of atoms of Pb/cc in Metallic Pb}}$$

$$= 0 \cdot 31 \times \frac{4 \cdot 70}{291} \times \frac{207}{11 \cdot 34} = 0 \cdot 09$$

The total absorption coefficient of lead azide of density $4 \cdot 70$ is therefore

$$0 \cdot 31 + 0 \cdot 09 = 0 \cdot 40 \ cm^{-1}.$$

This value can be combined with the known Roentgen dosage to give the amount of energy absorbed by each sample under irradiation. By definition, 1r is an amount of radiation corresponding to an absorption of $0 \cdot 11$ ergs per cc by dry air. The absorption coefficient of air for 650 kV radiation is $1 \cdot 00 \times 10^{-4} \ cm^{-1}$ so that the energy absorbed by lead azide per cc is given by:

$$\frac{0 \cdot 11}{1 \cdot 00 \times 10^{-4}} \times \frac{0 \cdot 40}{4 \cdot 70} \ r$$

$= 94r$ ergs/g. of PbN_6 where r is the Roentgen dosage. Samples 1 and 11 ($10^6 r$) should therefore have absorbed 94×10^6 ergs/g. (i.e. $2 \cdot 25$ calories/g.) and sample 22 ($6 \cdot 35 \times 10^6 r$), 600×10^6 ergs/g. (i.e. $14 \cdot 3$ calories/g.).

A consideration of the mechanism of the thermal detonation is outside the scope of this report and forms the subject of an experimental and theoretical investigation which is now being made (17). However certain points will be discussed here and in addition Part II 2 will show the relevance of these results to the general subject of the mechanism of the detonation of lead azide. Current theories of the decomposition of ionic solids emphasise the importance of lattice defects. In the thermal decomposition of barium azide Thomas and Tompkins (14) postulate a mechanism in which one type of defect, F centres, is made mobile by interaction with another, anion vacancies. The earlier theory of Mott had utilised mobile interstitial Ba^{++} ions. The mechanism of the thermal decomposition of lead azide has not yet been worked out but experimental results, (19) show that it is similar in type to that of barium azide i.e. it is a surface, interface reaction catalysed by nuclei of the metallic decomposition product. The mechanism may be similar to that for barium azide proposed by Thomas and Tompkins, or, in view of its relatively high ionic conductivity, the decomposition may follow a mechanism similar to that proposed by Mott. It is highly probable that, by analogy to the thermal decomposition, its thermal detonation also should be dependent upon lattice imperfections.

It is known (10) that irradiation of barium azide with ultra-violet light produces decomposition by an exciton mechanism and this gives a permanently increased concentration of anion vacancies. As a result a thermal decomposition carried out on pre-irradiated barium azide (14) proceeds much more rapidly than one carried out at the same temperature on unirradiated material. Similarly, it has been shown (11) that electron bombardment of barium azide produced decomposition by a mechanism dependent upon positive holes, which again gives rise to anion vacancies and increases the rate of a subsequent thermal decomposition. The effect of pre-irradiation and pre-bombardment on the thermal decomposition of lead azide has not

been investigated but Groocock (12) has shown that both irradiation and electron bombardment produce decomposition by a positive hole mechanism and it is highly likely that pre-treatment would accelerate a subsequent thermal decomposition.

As noted above, it is probable that the thermal detonation of lead azide has a mechanism dependent upon lattice imperfections and we should therefore expect that any pre-treatment which increases the concentration of whichever defect types are utilised in the detonation mechanism should sensitize the material. The sensitization produced in the sample irradiated at $6.35 \times 10^6 r$ is undoubtedly due to the high concentration of imperfections produced. As noted in the introduction the imperfections produced initially by the radiation will not include anion vacancies. However although no decomposition was measured during the irradiation it is almost certain that this did occur - irradiation of lead azide with ultra violet light and slow electron bombardment are known to give decomposition (12) and high energy X-irradiation of sodium azide gives decomposition (13). It is therefore likely that anion vacancies will be produced too and these are possibly the active defect, for positive holes and excitons are less likely to be permanent. Similarly excited states of the lead ions would be expected to return to the ground state on standing. The sensitization we have measured (and also the sensitization to decomposition measured by other workers) was permanent and must therefore be dependent upon imperfections of very long life. The colouration produced by the irradiation is further evidence for the production of imperfections by the irradiation, being due to the additional absorption bands in the visible region of the spectrum, associated with defects or colloidal lead.

A rough estimate of the number of positive holes produced can be made if it is assumed that the energy required is of the order of 30 ev which is the average value for pair production in air. The number of excitons produced is probably greater. For samples 1 and 11:

Energy absorbed $= 94 \times 10^6$ ergs $= 59 \times 10^{18}$ ev/gm.

No. of excitations $= \dfrac{59}{30} \times 10^{18} = 2.0 \times 10^{18}$

Total no. of ions per g. $= \dfrac{3 \times 6.02 \times 10^{23}}{291} = 6.2 \times 10^{21}$

Fraction excited $= \dfrac{2.0 \times 10^{18}}{6.2 \times 10^{21}} = \dfrac{1}{3.1 \times 10^3}$

For sample 22 this becomes $1/4.9 \times 10^2$. The quantum efficiency for the decomposition of sodium and barium azides by ultra-violet irradiation and by electron bombardment was of the order of 10^{-2} to 10^{-3}, so it is probable that the concentration of anion vacancies produced should be two or three orders less than the figures calculated above.

In reference 2 (page 235) an estimate is given of the dosage of gamma radiation received as a function of distance from a nominal 20 K ton bomb, and it is concluded that for distances of about 2,000 ft. the dosage is $10^4 r$ which is less than 1 per cent of the dosage we have found necessary to give an appreciable effect. At distances less than this complete destruction of any ordnance by blast and fire is to be expected. Even if γ-irradiation due to fall-out and also the effect of neutron bombardment is added no great effect on the sensitivity can be expected. It should be noted that even the highest dose irradiation ($6.35 \times 10^6 r$) gave a sensitization (on the minimum temperature for detonation criterion) that was small compared with that produced by a change in the type of α-lead azide. (Compare the results found for service α-lead azide, with those for pure α-lead azide, particle size 60 - 150 mesh - page 5.)

The energy carried by neutrons from an atomic explosion is only 1 per cent of that carried by γ-rays (2) and in general it is to be expected that it will produce similar kinds of defects in the azide. However, neutrons of thermal energy suffer an (n,p) reaction with nitrogen atoms and the transformation of the nitrogen atom to a carbon atom may produce special effects leading to sensitization. Also the ejected proton will give a much greater concentration of imperfections along its

path than γ-ray photons. Neutrons of high energy lose much of their energy by knock-on collisions with atomic nuclei and these displaced nuclei, produce very high concentrations of imperfections along their path. Moreover lattice vacancies and interstitial ions are produced in large numbers, and because of the very important part these particular defects are thought to play in the decomposition of azides special effects on the sensitivity might again be possible.

4. General Conclusions and Future Work

It has been shown that irradiation of service lead azide with high energy X-rays at dosages of less than 10^6r produces no noticeable sensitization to a thermal sensitivity test. Even at 6.35×10^6r the effect is small compared with that produced by a change of α-lead azide type. It is thought that γ-radiation dosages of a magnitude sufficient to produce a marked effect are unlikely to be found in the field at distances from an atomic explosion where complete damage is not produced by other effects.

It is suggested that, even though the total energy carried by neutrons in an atomic explosion is less than that carried by γ-rays, because of possible special effects, important in reactions of ionic solids and particularly nitrogen compounds, the effect of both thermal and fast neutron irradiation should be investigated experimentally.

An experimental and theoretical investigation of the thermal detonation of lead azide is being carried out. The effect of pre-irradiation with ultra-violet light and possibly pre-electron bombardment on the thermal detonation is likely to be of interest in this programme.

Part II

1. Sensitivity tests

1.1 General Analysis of Sensitivity Tests

For any explosive there is a certain probability that explosion may occur accidently during manufacture, transport, use etc. and in general terms it may be said that the sensitivity of an explosive is a measure of this probability. After several years of large scale use the sensitivity of any explosive can be assessed directly from the presence or absence of accidental explosions, but for a new explosive this experience has not been accumulated and it is necessary to have some other means of measuring its sensitivity so that a decision can reasonably be made as to whether it can safely be brought into use. The various empirical sensitivity tests that have been devised have this as their object. They try to place explosives in an order of "figures of insensitiveness" so that an estimate can be made of the accident probability of new explosives compared with explosives already in use. These sensitivity tests (e.g. impact tests, gap tests, friction tests) try to simulate the conditions which in practice lead to accidental explosions. The degree of violence with which the test must be performed on the new explosive to produce explosion is compared with the degree of violence necessary to explode an explosive of known sensitivity. It is found in practice that no certain conclusions can be drawn from a small number of measurements and it is only by a statistical analysis of a large number of measurements that useful information is obtained. This variability is a consequence of the great complexity of the processes leading to explosion in the performance of the tests, which is a reflection of a similar complexity in the processes actually leading to accidental explosions. Even the best sensitivity tests, which give results corresponding closely with later experience of actual use, are therefore time consuming and expensive.

It is probably impossible to obtain a single, quantitative measure of the sensitiveness of an explosive. In general every different explosive charge (the charge may be anything from a single crystal of initiator to a large casting of high explosive) will be either sensitive or insensitive to any particular action performed upon it, i.e. a particular action will divide explosive charges into two groups: one will contain charges sensitive to the action, being exploded by it, the other will contain charges insensitive to the action. Different actions will give a different distribution of charges between the two groups. Even with actions which differ only in the violence with which they are performed no definite conclusions

can be made without a knowledge of the mechanism leading to explosion. Similarly, different charges of the same explosive may show very different sensitivities to identical actions e.g. charges clear-cast from pure TNT are very insensitive to the action of even strong shock waves but charges pressed from small particle-size TNT are relatively sensitive to shock. Finally, there is no fixed criterion which fixes the "fire" condition in an explosion and in different circumstances this may be defined as detonation of a single crystal, propagation to the whole charge, rapid burning but without true detonation etc. In practice it would seem reasonable to fix the "fire" condition at the level where serious damage is produced by an accidental explosion and this will obviously vary from charge to charge. Particular charges showing a certain sensitivity to a particular action may show a different sensitivity to the same action if the "fire" condition is changed.

The mechanism leading to detonation in all sensitivity tests can be divided into three parts:

(i) an action is performed on the explosive charge

(ii) this produces a change in the physical state of the charge
     (e.g. the temperature of the whole or some small part of it is raised).

(iii) the "new" physical state of the explosive charge is such that a chemical reaction takes place which leads to detonation giving a "fire"; alternatively the chemical reaction, if occurring at all, does not lead to a detonation, giving a "no fire". (The "fire" condition can be defined in any way, e.g. as complete propagation, initiation of one crystal, etc.).

These three processes, while they must logically follow in the given order will in practice be largely concurrent and each one will react on the others. Further, each process will in general contain a number of variables, so that the overall system will be very complex.

A typical sensitivity test will now be considered in terms of this analysis, for example a friction test in which the explosive, mixed with grit, is ground between metal plates. Here the closest we can come to defining the action is to say that an ill-defined number of explosive particles has been placed in ill-defined proximity to a number of grit particles which have been heated to a number of different elevated temperatures. And further, the relative positioning of the grit and explosive particles and the temperatures of the grit particles will be varying in a complex manner with time during the test. To make the position even more complicated the action performed will depend upon the properties of the explosive. For example, one explosive might lubricate the grit particles so that no significant elevation of temperature of the grit is produced.

We see that for a test of this type the action performed is so complex that we cannot hope to get detailed knowledge of its effect. However, let us assume that we have full knowledge of the action performed; we can now consider section (ii). The new physical state of the explosive charge (its temperature and concentration distribution in space and time, etc.) will depend upon the action performed and the physical properties of the charge (the specific heat, the thermal conductivity, the hardness, the particle size and distribution, the state of aggregation, etc.). Once again, for the general case, the physical state of the charge will vary in a complex manner with time during the test and we have the further complication that the chemical reactions considered in (iii) will themselves influence the physical state (e.g. the heat of reaction produced will raise the temperature of the explosive). To avoid this latter complication a study in this section might best be carried out on an inert analogue of the explosive, of identical physical properties.

Carrying the analysis a stage further, when we have complete knowledge of the physical state of the explosive produced by the action we can now consider the chemical reactions leading to detonation. These may go through initiation and growth stages over a fairly long time period, during which the physical state of the explosive will be varying in a complex manner because of the continuing action, the various energy dissipative processes and the effects of the chemical reaction itself. The changing physical state will, of course, have its effect on the chemical reactions

Most empirical sensitivity tests even though they may give sensitivity values which correspond closely to the actual sensitivity found in use, have a complexity of this order and are therefore unsuitable for any detailed analysis.

It is seen that the sensitivity of an explosive charge under any particular test action is a complex of its physical and chemical properties. One explosive charge might be sensitive because the action produced a large change in its physical state. Another might be sensitive because only a small change in its physical state was needed to start a chemical reaction leading to detonation. A third might be insensitive because even though initiation of some part of it occurred, the arrangement of particles was such that propagation was inhibited.

1.2 Comparison of sensitivities of irradiated and unirradiated service lead azide

In this work we wish to compare the sensitivity of service lead azide irradiated with high energy X-rays, with that of unirradiated service lead azide. The irradiation is capable of altering both the physical and the chemical properties of the salt. In the introduction, reasons were given which suggest that quite large changes in the chemical properties might be expected, and among these are included the chemical sensitivity (part iii of the above analysis) and the explosive power. The latter will be reduced by any decomposition produced by the irradiation, but it is unlikely that more than a fraction of a percentage of the total material was decomposed by the dosages used, although this decomposition was not measured; the appearance of the irradiated crystals did not accord with any major decomposition. The chemical sensitivity, however, might be changed markedly.

The most important physical parameters that influence the chemical reactions leading to detonation are likely to be the same as those which most influence all chemical reactions, i.e. the temperature and the concentrations of the various reacting species (the latter will include concentrations of defects, surface ions, free radicals etc.) and their variations with time. For any given action the resulting temperature, concentration, time distribution will be influenced mainly by the thermal conductivity, specific heat and particle size and distribution (apart from changes produced by the resulting chemical reactions). For certain tests involving grinding, hardness will be important and for others involving electrical initiation the electrical conductivity may be important. The X-irradiation has no effect on the particle size of the service azide crystals and changes in other concentrations will be indicated by chemical effects. Of the other physical properties it is known that the thermal conductivity of ionic salts is reduced by irradiation, the defects produced reducing the mean free path of the phonons through the lattice. Similarly, irradiation changes the hardness by the production of dislocations and by the production of defects which serve to lock dislocations and inhibit their movement. The electrical conductivity may be reduced because of the discontinuities produced in the periodic field of the lattice reducing the mobility of electrons or increased because of the production of mobile charge carrying defects.

However, it would seem that the temperature, concentration, time distribution produced by the performance of any action on any charge made from either the irradiated material or the unirradiated material will be influenced mainly by the particular charge set up and the arrangement of the crystals (both of which are unaffected by the irradiation) and little affected by small changes in the internal physical properties of the crystals apart, of course, from the effect these changes produce in the chemical reactions. If this is true any differences in the sensitivity of charges made from the irradiated and unirradiated materials will be due entirely to the chemical changes of Section (iii) of our analysis, and only these need be considered.

Lead azide has the property of detonation at full velocity and power in very small charges (20). In fact it is only in single crystals of size less than 100 μ that full detonation does not occur. Initiation of a single crystal is usually sufficient to cause complete propagation with detonation of the entire charge. Comparison of the chemical sensitivities of irradiated and unirradiated single crystals otherwise identical should therefore be sufficient to compare the sensitivities of any identical charges made from these materials. In any case propagation through the charge will be governed only by its physical properties, and the power and sensitivity of its constituent crystals and if only the sensitivity is changed by irradiation the propagation should run parallel to the initiation.

Summing up, if a complete comparison of the chemical sensitivities (part iii) of two originally identical single crystals of Service lead azide, one irradiated and the other unirradiated, can be made, then the sensitivities to any identical action of any identical charges made from these two materials should run parallel to the single crystal sensitivities.

It has been noted above that it is likely that the chemical reactions leading to detonation, like other chemical reactions are governed mainly by (a) the temperature and (b) by the concentrations of the various reacting species. In a sensitivity test the performance of the action may alter several of the parameters that define the physical state of the explosive charge but only changes in the temperature and the concentrations will affect the subsequent chemical reactions. For most sensitivity tests the "new" physical state (prior to chemical reaction) produced by the action will have much the same concentrations of reacting species as those of the original physical state and it is suggested that usually it will be increases in the temperature of the charge or some part of it that will initiate the chemical reactions leading to detonation. This is not always true: in the detonation of lead azide crystals growing from solution, no appreciable temperature changes occur and here it may be the build up of the concentration of some reactive species in the solution or on the surface of the crystal, which leads to detonation. Similarly, the detonation of nitrogen tri-iodide by high vacuum treatment (21) is not a result of temperature changes, but because the concentration of surface ions free of adsorbed ammonia, is increased. However, these are exceptions and it is probably true that in most cases it is increases in the temperature of the explosive charge or some part of it that start and control the chemical detonation reaction. This will certainly be true for any sensitivity test working on a "hot spot" mechanism. It would seem therefore that a quantitative assessment of the thermal detonating properties of the irradiated and the unirradiated materials, is the most reasonable way of comparing their chemical sensitivities.

The ideal way of comparing the thermal detonating properties of the irradiated and unirradiated materials would be to get a number of identical crystals of the service lead azide and to irradiate some of them at the correct dosage leaving the others unirradiated. The temperature of one of each type of crystal is now raised to a particular value and maintained at this value until one or other detonates. If the irradiated crystal detonates first, then the irradiated crystal will be sensitive to an action that maintains the particular temperature for that time while the unirradiated crystal will not be sensitive to that particular action. The time to detonation of single, otherwise identical crystals of service lead azide, both irradiated and unirradiated at other temperatures would then be determined, covering the whole temperature range from that at which detonation did not occur to that at which detonation occurred in zero time. If the time to detonation/temperature curves were identical over the whole range, then it could be said that the chemical sensitivities were the same. If the time to detonation of the irradiated material at any temperature was always less than that of the unirradiated material, then it could be said that the irradiated material was sensitized over the entire range. If the curves crossed, then under some conditions there would have been sensitization and under others de-sensitization. For general applicability it would have to be assumed that these results obtained at constant temperatures could be applied to systems in which rapid variations of temperature occurred, and there seems no reason why this should not be so, for if it was shown that sample A was more sensitive than sample B both at temperature T_1 and at temperature T_2, then it would seem very unlikely that in a test in which the temperature varied between T_1 and T_2, that B would be found more sensitive than A.

The test carried out in practice falls short of the ideal outlined above. It is virtually impossible to obtain a number of completely identical crystals of service lead azide, but steps were taken to make the crystals tested as nearly as possible the same. They were all taken from the same, well aged batch of material. Then as crystal size is an important parameter a particular sieve fraction only was used and to reduce the effect of residual variations each sample tested was made up of a large number of crystals. The time to detonation of the most sensitive in each sample was then recorded and these are likely to be nearly the same. For suppose sensitivity ran parallel to crystal size, the largest crystal being most sensitive. If the size limits given by the sieves were 0·100 mms. and 0·120 mms. then each sample containing a large number of crystals would contain some which were negligibly different from the size limit of 0·120 mms. i.e. which had the highest sensitivity.

In practice this device will probably not work perfectly but it should reduce the scatter considerably. The use of this method introduces the possibility that detonation does not depend upon a single crystal, but upon interaction between two or more. This is unlikely because it would be mainly a self-heating effect and this did not occur to any great extent (see below). Moreover, if inter crystal action were significant the sensitivity would be a function of the sample size. This is contrary to experiment.

The graphs of time to detonation against temperature have been prepared on the assumption that the crystals remain at the furnace temperature until just before detonation. If this is not so the possibility of detonation of any crystal might be slightly dependent upon such things as its thermal emissivity and how good was the thermal contact it made with the copper block. However, conditions are ideal for reducing self-heating effects. The crystal is small and thus has a high surface to volume ratio and the surface is blackened by reaction products, so temperature equilibriation by radiation is facilitated. Further, equilibriation will be assisted by conduction to the copper block. From the known reaction rate just prior to detonation, and knowing the heat of reaction, the temperature rise produced by self heating can be calculated if some heat exchange condition is assumed. For black body radiation only (ignoring conduction) a very rough calculation indicates a temperature rise of the order of 1°C which is unlikely to be significant. Another approach would be to extrapolate the rate of decomposition curves for low rates to higher rates and see if there was any divergence between the theoretical and experimental curves, that could be attributed to self-heating.

In the ideal test, outlined above, the whole temperature range from the temperature giving no detonation to that giving detonation in zero time would have been investigated. In practice it has only proved possible to investigate part of this range because at high temperatures the time to detonation is so short that the heat up time of the crystal and the time lags of the recording system become significant. Conclusions drawn from this work and applied to sensitivity tests in which a high temperature is applied for a short time therefore involve an extra-polation, but unless there is a radical change of mechanism in different temperature regions there is no reason why pre-treatment giving sensitization at one temperature range should give no sensitization or de-sensitization at another.

This sensitivity test has been carried out on samples of lead azide that have been held in a high vacuum overnight. While it is unlikely that this treatment will have significantly altered the physical properties of the salt it is possible that quite large changes might be made in its chemical properties. It has been found, for example, that nitrogen tri-iodide detonates at room temperature in vacuo because vacuum treatment removes surface adsorbed ammonia, which stabilises the compound (21). However, both the irradiated and the unirradiated azide have been treated in the same way and it is probable that any effect produced by the vacuum treatment will be the same for both samples. This test could be modified to work in different pressure regions.

The general conclusion is therefore reached, that at the Roentgen dosage for which this test revealed no appreciable change in sensitivity, no other test carried out on our samples should reveal a significant change in sensitivity. It should be pointed out that this test indicated a large difference between two very similar materials (service α-lead azide and pure α-lead azide) so that, while it is possible that a test of even greater discrimination might show a difference in sensitivity where this test showed no difference, no practical advantage would be gained. The further conclusion is reached that for the Roentgen dosage where this test shows a difference in sensitivity other tests, if sufficiently discriminating, should reveal the same change. These two conclusions are based on the following assumptions, which have been discussed above:

(a) there is no significant difference in the physical parameters controlling energy transfers of the irradiated and unirradiated material;

(b) changes in the sensitivity to propagation run parallel to changes in sensitivity to initiation;

(c) the chemical processes leading to detonation in practice are temperature dependent and no other external physical parameter (e.g. pressure) has any significant effect;

(d) extrapolation of the results obtained over a limited temperature range to higher temperatures where times to detonation are short, can be made;

(e) the use of dynamic temperature conditions instead of this test's static conditions will not give special effects.

1.3 More general applicability of this test

In this work the test has been used exclusively to compare the sensitivities of irradiated and unirradiated service lead azide. Here the problem is relatively simple because identical physical properties can be assumed for any charges made from the two materials and from a knowledge of the chemical sensitivity immediate conclusions can be drawn about the total sensitivities of any otherwise identical charges, made of the two materials, to any action. For other materials these assumptions cannot be made so that, even if values of the chemical sensitivity (section iii) were obtained general conclusions about the total sensitivity could not be made without additional information about the physical properties.

In any detonation the "new" physical state (part ii of the analysis on page 10) of the explosive charge produced by the initial action (part i) will usually be only relatively little different from its initial state (e.g. a rise of 100 or 200 degrees in the temperature of some small part of it). On the other hand, the physical conditions in the reaction zone of the stable detonation which results will be much more extreme, these being produced by the energy liberated by the exothermic chemical reactions taking place. For the chemical reactions considered in part (iii) of the analysis there will in general be two possible mechanisms leading to the change from the "new" physical state to the detonation reaction zone physical state: (a) self-heating (b) some accelerating chemical reactions dependent e.g. upon autocatalysis. It is probable that most growths to detonation are influenced by both (a) and (b).

If the chemical reaction taking place in the explosive charge is not autocatalysed, i.e. the rate of reaction stays constant with time for any given physical state, except for the fall in rate as the quantity of reactant decreases, then there will be a certain rate of reaction associated with the "new" physical state. If the rate of energy production exceeds the rate at which it can be dissipated the physical state of the charge will become even more extreme by the process of self-heating and the chemical reaction will be correspondingly accelerated. Finally the stable detonation conditions will be set up when there will be equilibrium between the energy production and dissipation processes. The important feature of detonation taking place exclusively by mechanism (a) is that from the moment of performance of the initial action to the time at which stable detonation is established there must be a continuous rise in the physical conditions to make the chemical reaction accelerate. (This, of course, assumes that there is no large change in the external factors governing the energy losses during the process - it would be possible to cool the reaction, when at an advanced stage, back to an early stage and then again allow it to build up).

No reaction leading to detonation can take place entirely by method (b) because the change from the "new" physical state to the much more extreme detonation reaction zone physical state of necessity requires self heating. However, the experimental results of this work show that in the thermal detonation of service lead azide much of the chemical reaction leading to detonation can take place under constant physical conditions, self heating becoming important only at the very end, although the details of the autocatalytic process taking place during this period are not yet known. The process may depend upon the build up of a certain concentration of some species necessary to the reaction or possibly aggregation or diffusion to some special position, of a species already present.

For a detonation controlled entirely by self-heating, i.e. where the chemical reaction rate is constant in time for any constant physical conditions, determination of the rate of reaction for particular physical conditions is the only chemical information required (a curve of rate of reaction against temperature for the range

from zero rate to the detonation zone temperature would probably be most useful, and if the kinetics were sufficiently simple extrapolation might give a reasonable value of the rate at the higher temperatures). The acceleration of the reaction rate to its detonation value would then be controlled by the known reaction rate under any given physical conditions, the heat of reaction and the various physical parameters controlling energy transfers. Calculations of this type have been made recently by Cook (22) for a model system where simple unimolecular kinetics were assumed and application to several secondary explosives has been made. For an explosive of this type measurements of time to detonation, such as used in this work, would be meaningless. So long as isothermal conditions were maintained no detonation would occur and a detonation resulting from self-heating would be largely influenced by the physical factors controlling heat dissipation.

For reactions in which autocatalysis is important the kinetics must of necessity be complex, particularly as the reaction rate will vary with time even though the temperature and pressure conditions remain constant, so that calculations of the type discussed in the preceding paragraph may be impossibly difficult. However, for explosives of this type detonation may in practice be influenced to only a smaller extent by the physical properties of the material and the chemical sensitivity, possibly defined from the time to detonation/temperature curves, such as used in this work may have value. For this test both the heat-up time and the self-heating period, which will be influenced by the physical properties of the charge, must be negligible. These both require the charge to be very small so that the test is only applicable to explosives which will detonate in very small charges. The type of charge used would need careful attention; single crystals, crystal aggregates and tiny pressed pellets might be used.

While these limitations are important this test has two advantages over many other tests.

(a) It measures directly the temperatures and the times for which these must be applied to give detonation. It thus quantitatively follows the physical parameters which are probably most important in governing the chemical reaction leading to detonation.

(b) The action performed on the explosive is very simple and the "new" physical state of the explosive charge is known with precision, i.e. the original state with the temperature increased to a known value, and the new state is maintained constant with time. Further the new state produced in a charge made of any explosive is largely independent of any of the physical properties of the explosive, i.e. the temperature of the new state is independent of the specific heat, thermal conductivity etc. of the explosive.

(c) The reproducibility of the test is relatively high. The time to detonation at a particular temperature can be determined to $\pm$ 20 per cent by a single measurement. Moreover the times to detonation vary in a regular manner with temperature so that quite a small number of measurements are sufficient to define the time to detonation/temperature curves.

2. The Thermal Detonation of α-Lead Azide

As noted above an exhaustive discussion of this topic cannot be given now and this section will merely include a brief discussion of the problem and record some additional information which has been obtained from these X-irradiation results which, it is believed is relevant.

The initiation of the detonation in lead azide takes place very rapidly and no deflagration preceding detonation has been observed in experiments made to a time resolution of better than 10^{-6} seconds (23). This implies that there is a changeover in less than 10^{-6} seconds from the initial slow "isothermal" reaction taking place in the physical state of the lead azide under the test conditions (in our case this physical state is defined as single crystals in vacuo at c.315°C), to the detonation reaction taking place in the much more extreme physical conditions inside the detonation reaction zone. It should be noted that the "isothermal" reaction is the detonation reaction proceeding at the rate corresponding to the physical conditions of the test and is not necessarily the same as the thermal decomposition reaction

characterised by the rate of nitrogen evolution, which is occurring simultaneously.

There are two possibilities, (a) that the chemical reaction leading to detonation is the same as the thermal decomposition reaction, (b) that the two reactions are different. Hawkes and Winkler (1) support the first view, whereas Garner (24) has suggested a different mechanism. The thermal decomposition (see above, page 7) procedes by a mechanism of surface nucleation by the product lead, which catalyses the reaction. This is then followed by a penetration of the lead/ lead azide interface into the crystal. It should be possible for cases where fairly certain assumptions can be made about the energy losses of the decomposing crystal, to calculate the self-heating produced by the measured decomposition and to determine if acceleration of the rate to the detonation rate can occur in the 10^{-6} seconds available. For this mechanism, too, it would be reasonable to assume that detonation would occur when a given rate of decomposition had been reached, i.e. when the rate of energy production was at the critical value to produce self-heating in each case. Any deviation from this would be expected to be in the direction of requiring a higher decomposition rate at a lower temperature for in this case the heat losses would be slightly greater. In fact, the rate of decomposition just before detonation has been found (17) to vary in a random manner with temperature. This may, however, have been because the aggregate decomposition rate of all the crystals was being measured instead of the decomposition rate of the crystal whose detonation was subsequently observed.

If the detonation reaction is different from the thermal decomposition reaction it is not possible at the present time to formulate a mechanism. The following points are of interest however:

(a) The decomposition may have three functions. It may

(i) provide defects necessary to the detonation,

(ii) accelerate the detonation reaction by the self-heating given by the decomposition,

(iii) destroy so much of the available material during the detonation induction period, that detonation cannot occur.

(b) If, as seems likely, the detonation has a higher activation energy than the decomposition, the former will be favoured at high temperatures and the latter at low.

(c) The detonation process, may still be a surface reaction, or it may be a bulk reaction. Comparison of effects produced by pre-irradiation with X-rays, which produce bulk defects, and ultra-violet rays and low velocity electrons, which give surface defects, would be of interest here.

(d) The detonation reaction is dependent upon crystal size. This may be because:

(i) the decomposition, being a surface reaction, destroys the material (see "a" above) too rapidly in small crystals,

(ii) as the detonation process must be dependent to some extent on self-heating, in small crystals the energy losses during the time of heat up from the "isothermal" reaction temperature to the detonation reaction zone temperature, may be such that detonation does not occur,

All these effects should be clarified by a study of the thermal detonation of α-lead azide crystals, otherwise identical, but of different size.

The marked acceleration of the detonation reaction produced by the high dosage of γ-irradiation implies that, whatever the mechanism, it is dependent upon lattice defects. If the pre-irradiation merely increases the concentration of some defect which is present in the unirradiated salt, or is produced in the induction period it is to be expected that the pre-irradiation would change the pre-exponential term in the activation energy equation but not the activation energy value itself. This is in the equation:

$$t_D = A \exp \left(\frac{E}{RT}\right)$$

where t_D is the time to detonation

       A the pre-exponential term

       E the activation energy

       R the gas constant and

       T the absolute temperature

The results shown in Figs. III and IV in which t_D was plotted against T for the unirradiated material and that irradiated at 6.35×10^6r have been used to calculate A and E. Values of log t_D and 1/T were fitted to a straight line using the least squares method. The results obtained including the standard deviations are given in Table II. For comparison the values for pure, unirradiated α-lead azide of particle size 60 to 150 mesh, are included.

Table II

Azide type	Irradiation dosage	E(k cals)	log A
Service	0	53 ± 15	-
Service	6·35 x 10⁶r	86 ± 8	27 ± 12
Pure α	0	90 ± 8	28 ± 13

It is seen that the result is not conclusive, although the high values found for the activation energies are of interest. The large values of the standard deviation are due more to the narrowness of the temperature range investigated, than to lack of precision in the measurements.

Acknowledgements

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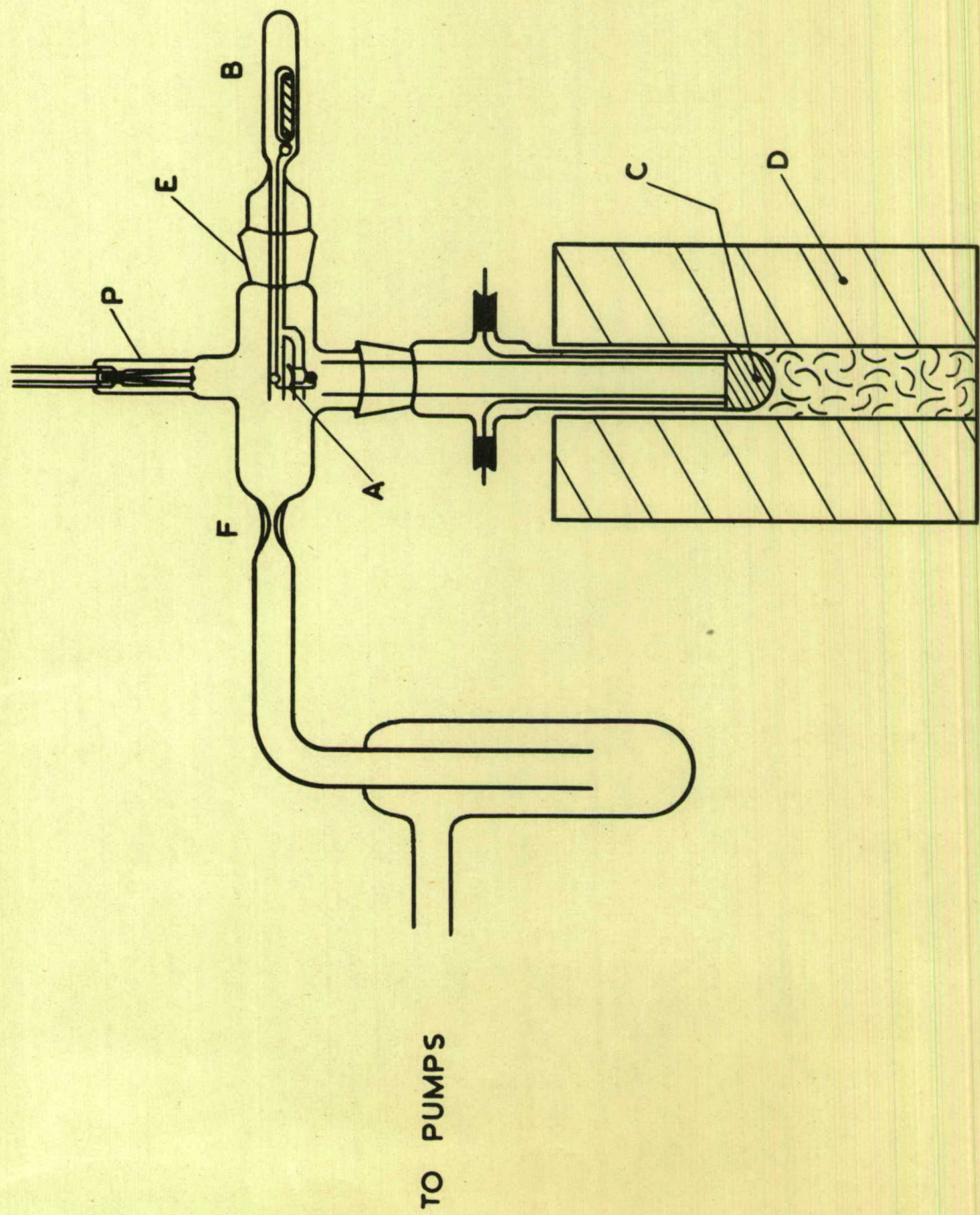24. W. E. Garner: Trans. Far. Soc. 34, 985, 1,008, (1938).
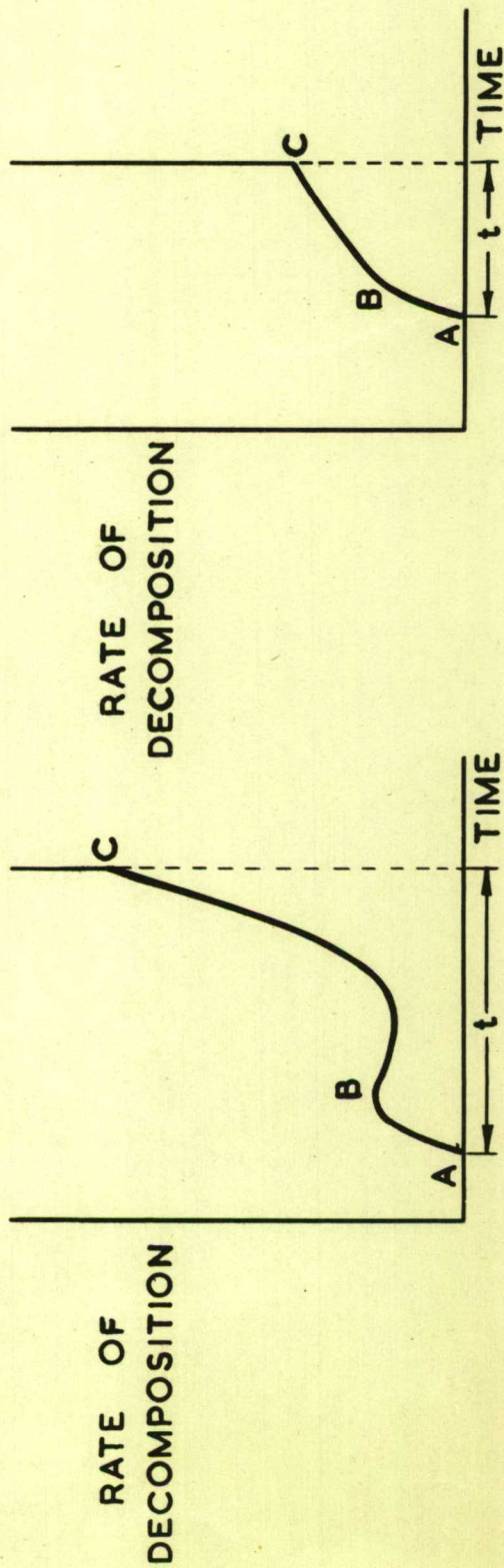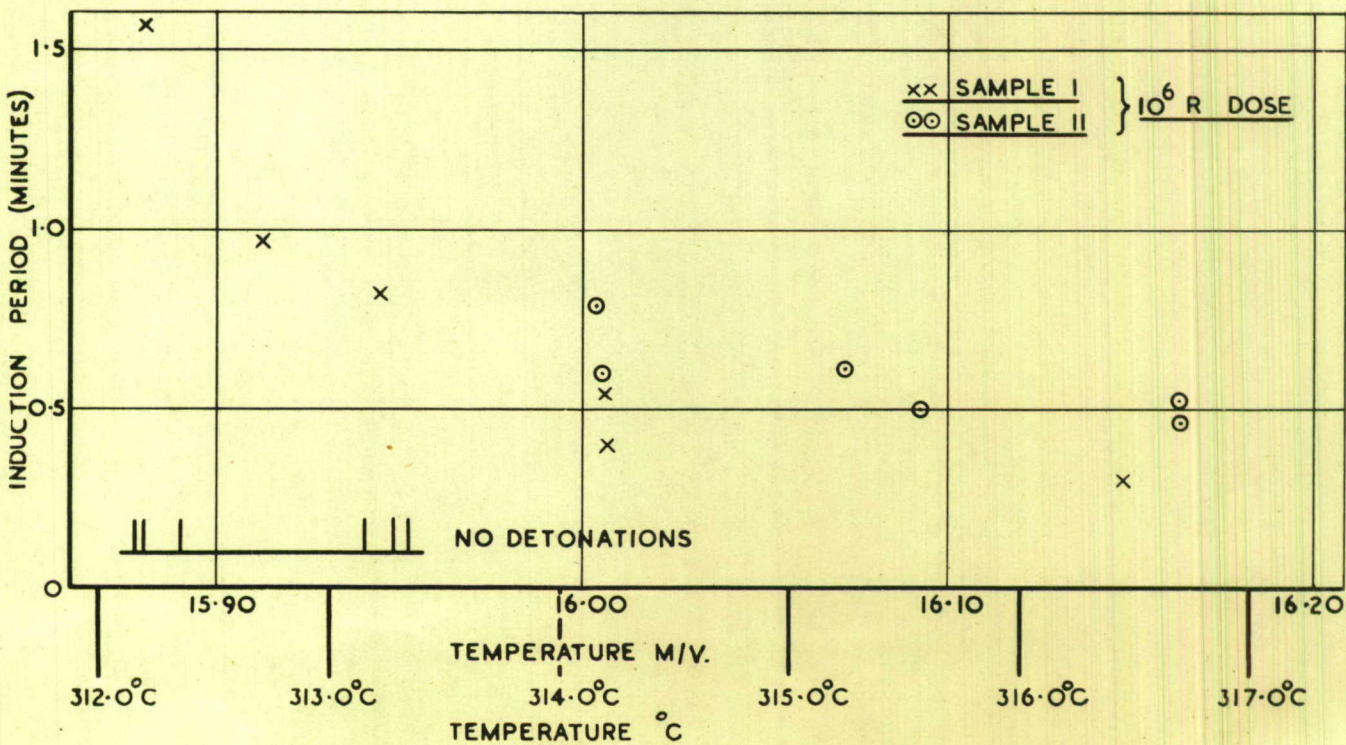
TO PUMPS

FIG I DIAGRAM OF TEST APPARATUS.
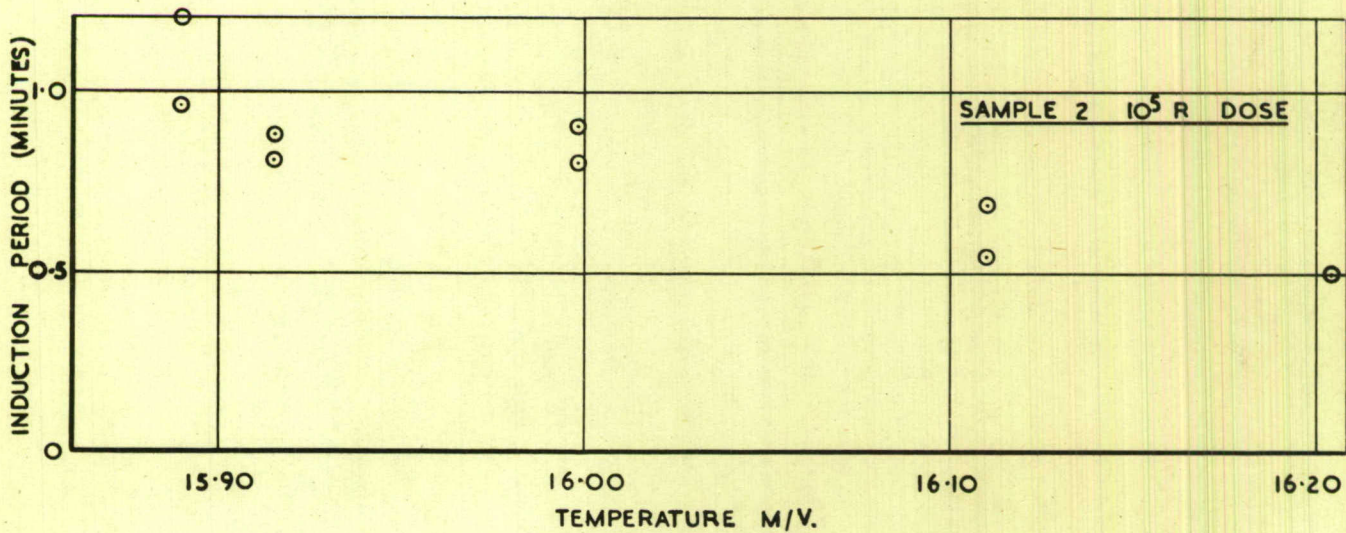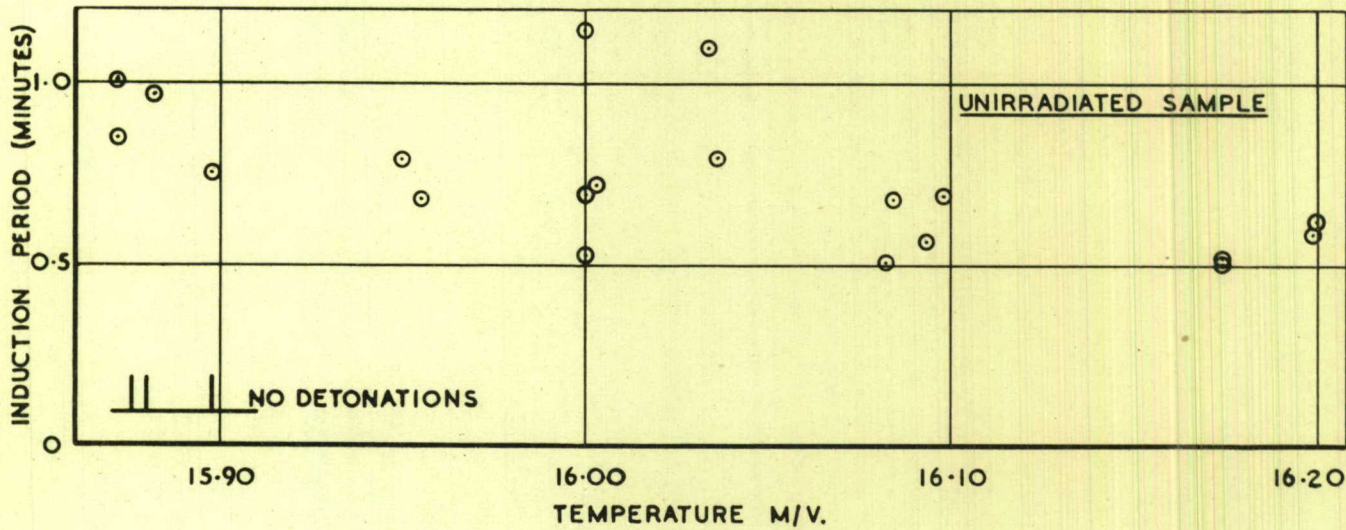
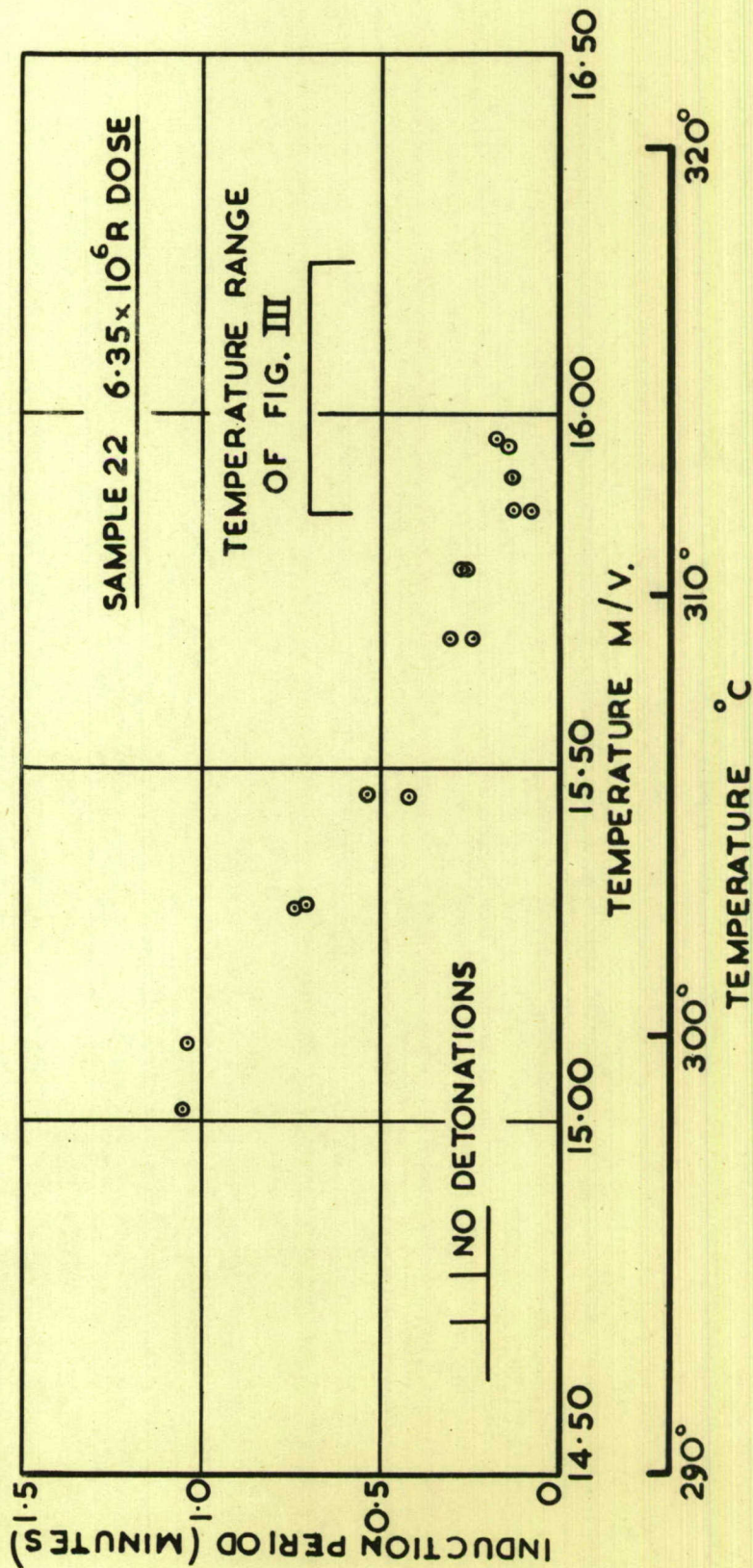FIGS. II (A. B.) PHOTOGRAPHIC RECORDS OF RATE OF DECOMPOSITION VERSUS TIME.

FIG. III TIME OF HEATING TO GIVE DETONATION VERSUS TEMPERATURE FOR IRRADIATED AND UNIRRADIATED SERVICE LEAD AZIDE.

FIG. IV TIME OF HEATING TO GIVE DETONATION VERSUS TEMPERATURE FOR

SERVICE LEAD AZIDE IRRADIATED AT HIGHEST DOSAGE.

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